OPTIMIZATION OF THERMAL CRACKING UNIT WITH AUTOMATIC HEAVY FUEL OIL STABILITY ANALYZER

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ABSTRACT

The main target in optimizing the thermal cracking unit is to maximize the yield of the valuable lighter intermediate distillates. The cracking process is then running as near as possible but still on the safe side of the severity limit resulting stable fuel oil. Stability or long storage life is an important factor demanded of heavy fuel oils refined in the thermal cracking/visbreaking production units. The stability figure for heavy fuel oils indicates the precipitation tendency of asphaltene molecules in the oil. The stability parameters (P-value, toluene or xylene equivalents) are usually determined by the manual spot test method using visual detection. However, these tedious manual methods take up to hours to perform.

PORLA, an automatic stability analyzer for heavy fuel oils[1,2] was developed and has been used for several years by a Finnish oil company Neste Oy. The stability analyzer performs the same stability measurement procedure (determination of P-value) as the manual method only in few minutes. The laboratory model of the instrument is now commercially available and it has also been tested in the laboratories of other oil companies. There is a good correlation between the results obtained by the analyzer and those by the manual method. The automatic stability analyzer brings with a cost-effective and reliable tool for optimization of thermal cracking processes and blending of heavy fuel oil components.

INTRODUCTION

An important prerequisite for the hassle-free use of heavy fuel oils is that there exist no precipitate formation during their storage and use. The formation of the precipitates in oils is a consequence of flocculation of the asphaltenes present in the oil. The amount and quality of asphaltene particles in the oil and the production conditions determine the tendency for asphaltene precipitation. The stability figure is depending on quality of the feed stock, the reactor temperature and reactor residence time. Stability figures (P-value, peptization value, xylene or toluene equivalent) all describe the precipitation tendency of the asphaltenes. One of the stability figures p value is an abstract real number varying between 1 and 6.

In oil refining, the thermal cracking processes are adjusted such a way that the bottom products are always stable. The optimal temperature of thermal cracker unit is decisive. The profitability of thermal cracking unit improves as the quantity of valuable middle-distillates such as light fuel oil and diesel fuel components increase. The yield of these components is maximized by control of process temperature. If the process temperature is too low, part of the middle-distillates remain in the heavy fuel oils and production is not optimal. If again the process temperature is too high, that results in unstable products, which will sedimentate during storage or upon mixing with other oils.

In general, when the stability figure is about two the production economics is optimized; the yield of the valuable light and middle-distillate components are maximized and the heavy fuel oil is still stable without any remarkable addition of expensive "solvents" (light gas oil components). P values near 1 mean unstable products.

However, the optimal P-value for each process varies, because the products can be used for different applications. For some applications, however, a sufficient P-value for the product is even 1.5 and in some applications it must be near 2, it depends on the blending. In case of e.g. marine applications, where wide range of blending may take place, the sedimentation of aphaltenes may result in engine problems due to clogging of ship's fuel system (separators and filters). To prevent asphaltene precipitation in oil products refined at too high temperature, "solvents" have to be added. Solvents are however expensive and production economy suffers. Therefore, the range between 1.5 and 2 is the area where the optimization of the process and the product with help of the P-value determination can bring huge amounts of money to oil refining companies. 0.5 P-value units may mean millions of US dollars annually, depending on the capacity and feed stock of the refinery. The P-values above two mean "too good" products which will seldom cause any stability problems, but that is at the expense of the production economy.

In practice, the optimal process temperature of thermal cracker unit is set at safe distance from, but as close to the upper temperature limit as possible. The automatic stability analyzer method, which gives the stability figure in few minutes, will be presented. The instrument was developed to replace the tedious manual methods in order to regulate the optimal process temperature especially when changing the feed stock in the production.

EXPERIMENTAL

Determination of stability figures

The stability parameter is usually determined by manual spot test method using visual detection. In order to adjust the viscosity of the heavy fuel oil sample be aromatic solvent like xylene or toluene is added. The asphaltenes in the heavy oil sample are precipitated by gradual addition of paraffinic solvent like n-heptane, decane or iso-octane. When subsequent amount of paraffinic solvent is added the oil becomes unstable and asphaltenes precipitate. After each addition of paraffinic solvent a droplet of the solution is placed on a filter paper and the visual detection of the two dark rings within each other formed in the spot indicate the precipitation. The stability parameter is determined from the amounts of oil, paraffinic and aromatic solvents. This manual test procedure takes from one to two hours to perform.

The function of an automatic computer controlled analyzer is based on the same procedure as the manual method, and the optical detection of precipitation point of asphaltenes during the measurement procedure is based on the scattering of visible light. At the precipitation point the intensity of scattered light rapidly increases. The analyzer gradually adds the selected paraffinic solvent in the prediluted heavy fuel oil sample, detects optically the precipitation point of asphaltenes and finally calculates the stability figure (P-value) on the basis of mass of the oil and the volume of aromatic solvent and paraffinic solvent consumption. To calibrate the instrument, three different dilutions from a heavy fuel oil with known P-value are first run by the instrument. Typical oil/aromatic solvent ratios are 4/1, 4/2, 4/3. The stability figures of these three solutions are applied in extrapolation procedure, where the impact of aromatic solvent to the solubility of asphaltenes is eliminated.

When all three solutions have been run by the analyzer the consumption of paraffinic solvent e.g. heptane of the undiluted heavy fuel oil sample X_0 can be extrapolated with the following way[3]:

$Y = $ xylene (ml) / [xylene (ml) + n-heptane (ml)]

$X = $ oil (g) / [xylene (ml) + n-heptane (ml)]

Figure 1 schematically illustrates the extrapolation procedure based on the titration of the three dilutions resulting paraffinic solvent consumption of an undiluted oil sample. Consequently, the stability figure P-value is calculated from the following equation:

$$P = 1 + 1/X_0,$$

where X_0 is the intersection of x axis and the straight line extrapolated via the three data points.

Correlation of P-value and toluene/xylene equivalents

In addition to the P-value, other methods like toluene and xylene equivalents are used to determine the stability of heavy fuel oils. Toluene and xylene equivalents are equal, the only difference between these two methods is the solvent (toluene/xylene). Toluene equivalent is determined by a method where the heavy fuel oil sample is first mixed with toluene typically in the proportion of one to five. Paraffinic solvent is gradually added in the mixture. After every paraffinic solvent addition a droplet of the mixture is taken and placed on a filter paper until separation of the spots appear. The toluene equivalent is the lowest toluene concentration (expressed in vol-%) of the solution where the asphaltenes are not precipitated[3]. The toluene/xylene equivalent is calculated in the following way:

Tol-eq. ={toluene (ml) / [toluene (ml) + n-heptane (ml)]}*100 %

When comparing the equation for the calculation of toluene equivalent and that one for the Y axis of the P-value determination the correlation between P-value and toluene equivalent can be seen. Figure 2 illustrates this linear correlation.

RESULTS

In an eight months laboratory monitoring test carried out by Scanraff refinery in Sweden[4] almost one hundred heavy visbreaker fuel (Vistar) oil samples with same origin were analyzed both manually and automatically with the analyzer. One objective of this test was to check correlation between the analyzer and the manual spot test method in the oil quality control laboratory use. The original values of this test period can be seen in Table 1. Fig 3 shows the stability figures for product "Vistar" obtained by PORLA and the deviations from the manual method during the monitoring period. 73 samples of 93 gave exactly the same stability figure by both methods, 8 samples gave 0.1 P-value unit higher value and 12 samples 0.1 P-value unit lower value by the analyzer than by the manual method. The statistical testing of the analyzer during over decade's constant use in refinery laboratories has proven the repeatability of the analyzer to be ±0.05 P-value unit. The test run result confirmed our repeatability results.

The results obtained by manual and automated methods did not significantly differ from each others. This is shown on the basis of the statistical tests carried out from the original data of Table1. The statistical tests done were F-test (Two-Sample for Variances), t-test (Paired Two-Sample for Means) and Friedman test (Repeated Measures Analysis of Variance on Ranks).

Probability value 0.40 of F-test shows variances to be equal. Paired t-test of which critical t-value was $1.98_{0.05}$ gave t-value 0.61 and probability 0.53. To confirm the test results obtained by F-test and t-test the Friedman test (Repeated Measures Analysis of Variance on Ranks) was performed. Table 2 shows and figure 4 illustrates the result of Friedman test. The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference between manually and automatically obtained results of P-values.

Especially the process temperature affects the formation and precipitation tendency of asphaltene particles. It is essential to control the reactor temperature of a thermal cracker production unit to such a level, where the heavy oil produced is still stable and there is no coke formation in the reactor tubes. A typical correlation between the temperature of thermal cracker reactor and the stability figure (P-value) for certain crude oil feed stock is illustrated in figure 5. The optimum reactor temperature, however, may vary according to the feed stock material and therefore it is important to detect for every feed stock the stability limit, which corresponds the highest temperature, where the production is on the safe side, where the product is stable and as near as possible to the severity limit in order to optimize the yield of the valuable lighter products and to avoid coke formation, which may lead to interruption of the production.

CONCLUSIONS

The optimization of thermal cracker units and the quality control of heavy fuel oil production can be improved as minimized off-spec production by an automated stability analyzer. Additionally, the use of an automatic analyzer brings with remarkable labor cost savings in an oil quality control laboratory compared to the tedious manual methods. Besides, the automated analyzer minimizes the errors due to differences in individual human capabilities for visual detection of spot test.

An automated stability analyzer developed at Neste oil refinery in Finland is based on this manual test method, but it performs the same procedure automatically in few minutes. It has been developed in order to save oil refinery laboratories' labor costs and to improve the handling of heavy oil stability and quality control.

It is known that the wider the dissimilarity between the blend components, the greater is the risk of incompatibility and possible often significant economical consequences. This automated method can be used also for detecting the stability figure of heavy fuel oil blends i.e. binary or ternary systems. Some stable products may form an unstable blend. Therefore, it could be reasonable to check beforehand the stability of such blends by making stable/unstable maps for binary or ternary heavy fuel oils systems.

Statistical calculations of the Scanraff's test run results indicate that there are not statistically significant differences between the result obtained by the manual and automated method. The small differences in the results is if anything due to random sampling variability. Therefore, the automatic method offers an fast, cost-effective and reliable tool to replace the tedious manual methods for analyzing the stability figure of heavy fuel oils.

REFERENCES

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TABLE 1. Stability figures P-values obtained manually and by automated PORLA analyzer during eight months test period at Scanraff, Sweden.

Manual	Automat	Manual	Automat	Manual	Automat	Manual	Automat
1.7	1.7	2.0	2.0	2.0	2.0	2.0	2.0
1.9	1.9	2.1	2.0	2.0	2.0	2.1	. 2.1
1.9	2.0	2.4	2.3	2.0	2.0	2.0	2.0
1.8	1.8	1.9	1.9	2.0	2.0	2.0	2.0
1.8	1.8	2.5	2.5	2.0	2.1	2.1	2.1
1.9	1.9	2.1	2.1	2.0	2.0	2.1	2.1
1.9	2.0	2.6	2.6	1.8	1.8	2.1	2.0
2.0	1.9	2.0	2.0	2.0	2.0	2.2	2.2
2.1	2.0	2.0	2.0	1.8	1.8	2.3	2.4
1.7	1.6	2.0	2.0	2.0	2.0	2.0	2.0
1.6	1.6	2.0	2.0	2.1	2.1	1.9	1.9
1.6	1.6	2.1	2.1	2.0	2.0	2.1	2.1
2.3	2.2	1.8	1.7	1.9	1.9	2.1	2.1
1.6	1.6	1.8	1.7	1.9	1.9	2.0	2.1
1.6	1.6	1.9	1.9	1.7	1.8	2.1	2.1
2.2	2.1	1.8	1.8	1.9	1.9	2.1	2.1
2.2	2.2	1.8	1.8	1.9	1.9	2.1	2.1
1.9	1.9	2.0	2.1	1.7	1.7	2.0	2.0
2.1	2.1	2.2	2.1	2.0	2.0	2.1	2.1
2.1	2.1	1.9	1.9	2.0	2.1	2.0	2.0
1.9	1.8	1.8	1.8	2.3	2.3	2.1	2.1
2.2	2.2	1.8	1.8	2.0	2.0		
2.1	2.1	2.1	2.1	2.0	2.0		
2.2	2.2	2.0	1.9	2.0	2.0		

TABLE 2. The results of Friedman test from the values of table 1.

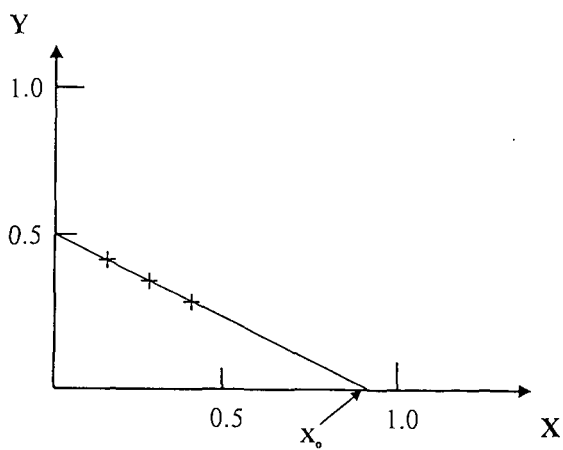| Group	Median	25 %	75 %
Manually	2.0	1.9	2.1
Automatic	2.0	1.9	2.1
Chi-square = 0.667 with 1 degrees of freedom. (P = 0.4142)			

FIGURE 1. Determination of paraffinic solvent consumption for an undiluted heavy fuel oil sample X_0 by extrapolation.
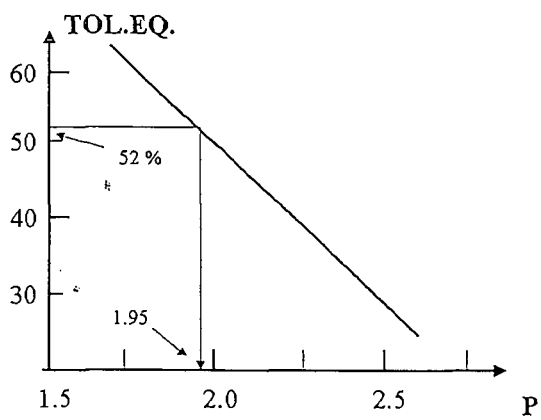
Figure 2. Linear correlation between toluene equivalent and P-value for heavy fuel oils.
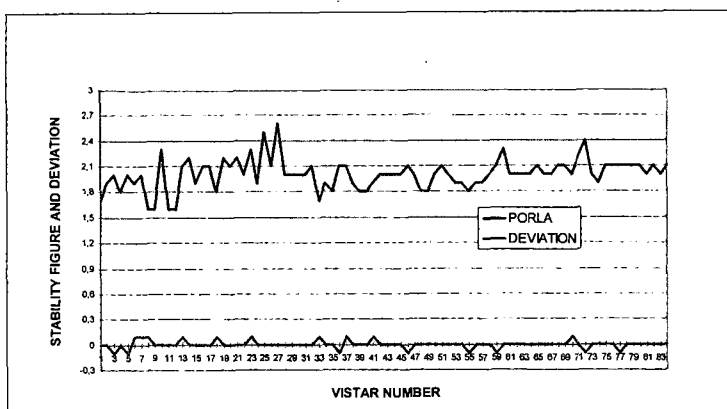
FIGURE 3. Stability figures of Vistar heavy fuel oil product obtained by PORLA analyzer and deviation of each value from the manually obtained value.
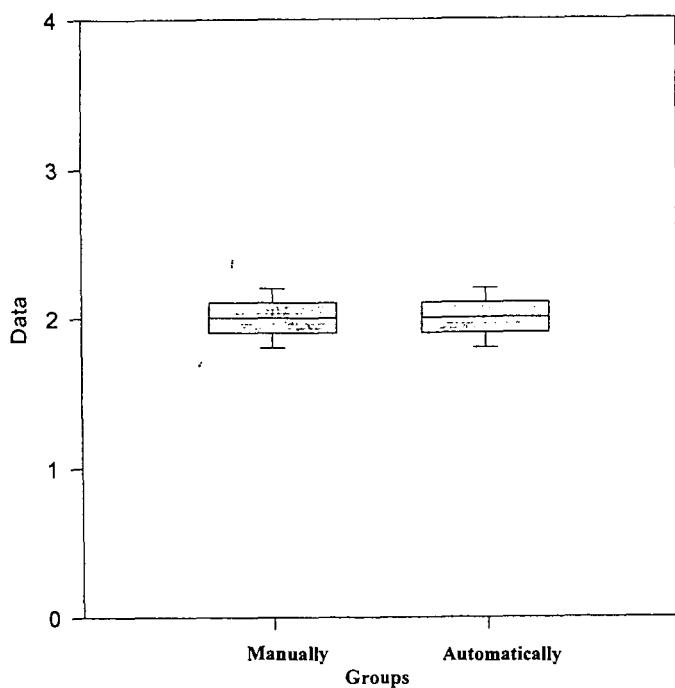
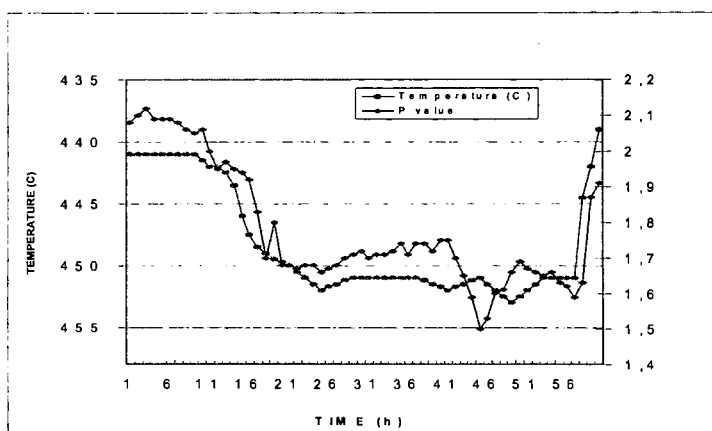FIGURE 4. A graphical illustration of the result of Friedman test carried out from the data of table 1.

FIGURE 5. Correlation between stability figure and thermal cracking process for certain feed stock material.